

NPS ARCHIVE
1997.08
KATCHARIAN, H.

DUDLEY KNOX LIBRARY
NAVAL POSTGRADUATE SCHOOL
MONTEREY CA 93943-5101

DUDLEY KNOX LIBRARY
NAVAL POSTGRADUATE SCHOOL
MONTEREY CA 93943-5101

**Risk-Based Corrective Action (RBCA) at Petroleum Contaminated Sites:
The Rationale for RBCA and Natural Attenuation**

by
Hope Katcharian
//

Submitted in Partial Fulfillment
of the Requirements
for the Degree of
Master of Science in Civil Engineering
August 1997

ENCE 799
University of Maryland
August 4, 1997

NPS Archive

1997.08

Katcharian, H.

~~1005~~
~~K/518~~
~~C.1~~

DUDLEY KNOX LIBRARY
NAVAL POSTGRADUATE SCHOOL
MONTEREY CA 93943-5101

Table of Contents

I. Introduction	
A. Background	1
B. Rationale	2
1. Costs	
2. Fixed cleanup threshold/varying risk	
C. “Acceptable” Risk	5
D. Cleanup Standards	6
II. Risk-Based Corrective Action	7
A. Summary of the LLNL Report	10
1. Findings/Conclusions	
2. Recommendations	
B. Public/Agency Response to the LLNL Report	13
1. SWRCB	
2. Santa Ana	
3. Distrust	
C. DoD Petroleum Hydrocarbon Cleanup Demonstration Program	15
D. MCAS El Toro	17
1. Background	
2. Environmental Setting	
3. Site Characterization, Site 390	
III. Natural Attenuation	20
A. “Nondestructive”/Physical Transport Processes	24
B. Physical Properties affecting transport	26
C. Biochemical transformation	28
1. Petroleum-degrading microbial population	
2. Soil factors affecting biodegradation	
3. Petroleum product chemical structure and its effect on biodegradation	
IV. Conclusion	38
A. Maryland	
B. Over the horizon	

Endnotes

Complete References

Figures and Tables

Figure 1: Flow Diagram for Risk-Based Corrective Action	8
Figure 2: Benzene Biodegradation Reactions	29
Figure 3: Reported Range of Empirical Biodegradation Rates	33
Table 1: Theoretical Residual Hydrocarbon Concentration	24
Table 2: Genera of Hydro-carbon-Degrading Bacteria and Fungi	31
Table 3: Typical Composition of Bacterial Cells	35

Appendix A

Site Conceptual Exposure Scenario under Current Conditions
Site Conceptual Exposure Scenario under Possible Future Conditions

“Muck and truck” is an expression often used to describe the excavation and hauling of petroleum-contaminated soils to a suitable disposal area. While this particular phrase reflects only one method for cleanup, it suggests a hasty and unconstrained approach to corrective action at petroleum release sites. Regardless of what the name implies, aggressive and possibly excessive cleanup activities aimed at protecting human health and the environment have resulted in profuse financial expenditures across the country.¹

...so write Dennis Rounds and Paul Johnson, two of the key drafters of the American Society for Testing and Materials’ new Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites, ASTM Standard E 1739.²

I. Introduction

I. A. Background

Risk-Based Corrective Action (RBCA) is a new phrase heard among engineers, researchers and regulators in the environmental remediation field. The phrase and acronym, pronounced like the name “Rebecca”, represent a more enlightened, perhaps mature approach to old problems. RBCA is not a new technology but rather a formal framework for decision making when planning environmental remediation goals. I restrict my discussion to RBCA as applied to petroleum contaminated sites because they have recently emerged as the newest testing ground of the RBCA concept.

Clearly, the key to developing objective cleanup criteria for soil and water remediation is to focus upon risk assessment. However, unlike polychlorinated biphenyls, dioxin and lead, whose soil cleanup criteria *were* developed based upon their associated risks, cleanup criteria for petroleum contamination is generally *not* based upon human health risk. Instead, the criteria are almost as varied as the states that developed the standards. In 1991, a survey revealed that 42 out of 50 states utilize the measure of total petroleum hydrocarbons (TPH) in

regulatory oversight and that soil cleanup goals spanned a range of 10 to 10,000 parts per million (ppm) TPH.³

This is not to say that we should develop national remediation goals. In fact, if we developed a single remediation standard despite differing site conditions, reuse scenarios, and petroleum products, the resultant risks would vary greatly. In some cases we would remediate sites with no measurable benefit (in terms of risk reduction) and in other cases we would not remediate to necessarily protective levels. Therefore, if regulators, engineers, risk assessors and toxicologists agree that fixed remediation goals are unacceptable, then perhaps they can also agree on a consistent, simple process to determine site-specific cleanup goals.

In addition to the above, there are numerous other reasons that the United States' regulatory policies should shift toward Risk-Based Corrective Action (RBCA). The most compelling ones are scientific advances in quantifying risks, a growing understanding of chemical compound fate and transport mechanisms and rates, changing ideas about "acceptable risk" in view of background risks, and the exceedingly high cost of remediation relative to the human health and environmental benefits. This paper takes a somewhat broad perspective because I believe that technical solutions must be evaluated in public health and regulatory contexts

I. B. Rationale

I. B. 1. Costs

As the December 22, 1998 deadline for upgrading underground storage tanks (USTs) approaches, the remediation market for leaking USTs has been thrown into flux. Less than

half of the 2.2 million USTs regulated by EPA have been upgraded or closed since this regulation went into effect eight years ago. Yet, state's trust funds are depleting and regulator case loads are high. Recent estimates place the cost of remediating underground storage tanks under current varying state guidelines from 19 to 45 billion dollars nationally.⁴

In California alone, the average cost to remediate a former UST site is \$150,000. As a result, the state started taxing each gallon of gasoline as a source of state funding to assist in clean-ups. By January 1996 the fund had spent \$200,000. It is expected to collect 1.9 billion dollars by the time the tax expires in 2005, \$600 million short of the estimated cost to remediate all of the USTs in California that exceed current regulatory thresholds.⁵

Even the most financially efficient remediation technologies are costly relative to the risk posed by the petroleum contamination. The cost of operating bioremediation facilities to clean hydrocarbon impacted soils, for example, is estimated at \$25 to \$33 per ton, depending upon regulatory requirements and other variables. This average is in addition to the construction costs which range from 350 to 500 thousand dollars for a biocell capable of remediating 1,200 tons per cycle.⁶

I. B. 2. Fixed cleanup threshold/varying risk

Beyond the monetary costs of cleanup, there is a more compelling reason that states should move toward a risk-based decision framework. The obviously flawed logic inherent in *uniform* concentration-based remediation goals at *varying* sites demands attention. Differences between sites, including land use, soil types, depth to groundwater and other environmental

factors, can result in significantly varied human and environmental health risks with similar contaminant concentrations in the soil.⁷ These uniform goals have been used in the past because they provided an easily applied standard that required little site assessment and nominal flexibility to owner's and regulators alike. Site-specific soil remediation goals, however, while more costly to develop and manage, provide for differences in site and exposure conditions.

Likewise, the traditional approach for handling groundwater contamination assumed that (1) all groundwater is potable, (2) it can be used anytime, and (3) that regulatory agencies should therefore require groundwater to be cleaned to drinking water standards everywhere. This approach is not always appropriate. All groundwater is not potable and all contaminated groundwater cannot be economically or technologically treated to drinking water standards. California prohibits cost considerations from compromising public health or the environment but it does recognize that the state and its regulated community have a finite number of resources. These resources and the state's efforts, therefore, should be focused upon sites with the greatest current or reasonably foreseeable future risks. Again, this is the principle that supports consistent application of the RBCA process.

In their article in *The True State of the Planet*, Ames and Gold poignantly remark that "risks compete with risks: society must distinguish between significant and trivial risks. Regulating trivial risks ...can harm health by diverting resources from programs that could be effective in protecting the health of the public."⁸

I. C. “Acceptable” Risk

At the same time that the high cost of cleanup is spurring the move to RBCA, regulators and scientists are questioning the methods of determining “how clean is clean”. In a presentation to the 84th Annual Meeting of the Air and Waste Management Association, Kathryn Kelly explored the origins of 10^{-6} as a criterion of “acceptable risk”. The 10^{-6} criterion represents the quantification of acceptable *excess* cancer risk, where “excess” represents the added or incremental risk associated with a carcinogenic contaminant above known or presumed background risks of developing cancers. Surprisingly it has been widely used for over 30 years but acceptable risk was not quantified or referenced in any federal *environmental* guidance until 1986.

The use of 10^{-6} began in 1973 in a notice in the Federal Register. The U.S. Food and Drug Administration (FDA) identified it as a screening level in proposed animal drug residue regulations to represent *de minimus* or “essentially zero” risk. The first environmental regulatory reference was in the 1986 Superfund Public Health Evaluation Manual which stated, “...remedies considered should reduce ambient chemical concentrations to levels associated with a carcinogenic risk range of 10^{-4} to 10^{-7} .”⁹ The follow on document, the 1990 National Contingency Plan, superseded the former and modified the risk range to 10^{-4} to 10^{-6} .¹⁰

The expression *de minimus* is an abbreviation of the legal concept “*de minimis non curat lex*” or, translated, “the law takes no account of trifles” ...Therefore, what began as an identification of trivial risks, somehow, over time, became the definition of maximum acceptable risk.

The quantification of excess carcinogenic risk itself is typically based on linear extrapolation of very high doses in rodent species to low-level exposure in humans. These extrapolations cannot be verified, but scientific consensus is that they are very conservative extrapolations, adding in safety factors for any number of variables.

Finally, we must recognize that risk is a function of toxicity and exposure. Before we can determine cleanup standards we must set an acceptable risk level, determine the extent of human exposure (or the exposure to the most sensitive species in the environment) and solve for the maximum concentration of chemicals that may remain in the environment and still present risks less than or equal to our “acceptable” risk.

I. D. Cleanup Standards

In California, remediation standards have usually been based on either the Maximum Contaminant Levels (MCLS) for drinking water, the State Water Resources Control Board’s (SWRCB's) nondegradation policy standards, or the California Leaking Underground Fuel Tank (LUFT) Manual. The Lawrence Livermore National Laboratory (LLNL) report advocates avoidance of these strict cleanup parameters, recommending instead that California employ a RBCA decision making framework consistently throughout the state. In fact, there is much argument that cleanup standards are best derived by evaluating the potential risks to human health and the environment that would remain at the site after remediation is complete.¹¹ This illustrates the importance of using site specific factors to develop cleanup levels. The potential risks should consider the potential fate of the contaminant, whether it is transported or transformed, and the potential pathways and receptors. Once all exposure

scenarios are investigated, the most restrictive concentration for each chemical of concern should drive the cleanup level.

U. S. EPA also supports development of risk-based decision making standards except where drinking water is affected. In those cases, EPA still prefers the MCLs as the standard of choice for clean-up thresholds.

II. Risk-Based Corrective Action

Because of these high costs of remediation and more current scientific assessments of risk, some states are turning to RBCA standards to systematically address leaking underground storage tank sites. The RBCA concept is multidimensional, it has been described as a compilation of toxicology, environmental management, risk assessment, risk management, environmental engineering, hydrogeology, and biology. Essentially it is a systematic framework for environmental decision making that relies on multiple disciplines for its development. Figure 1 is a flow-chart representation of the RBCA process.

Following along with figure 1, the RBCA process can be briefly explained with a description of the three-tiered process. The first step in RBCA is to conduct a qualitative risk assessment based upon general site assessment information. This identifies the contaminant source or sources, and current or reasonably expected future pathways. The contaminants and pathways are then evaluated in the context of potential human and ecological receptors and compared to a table of risk-based screening levels (RBSLs).

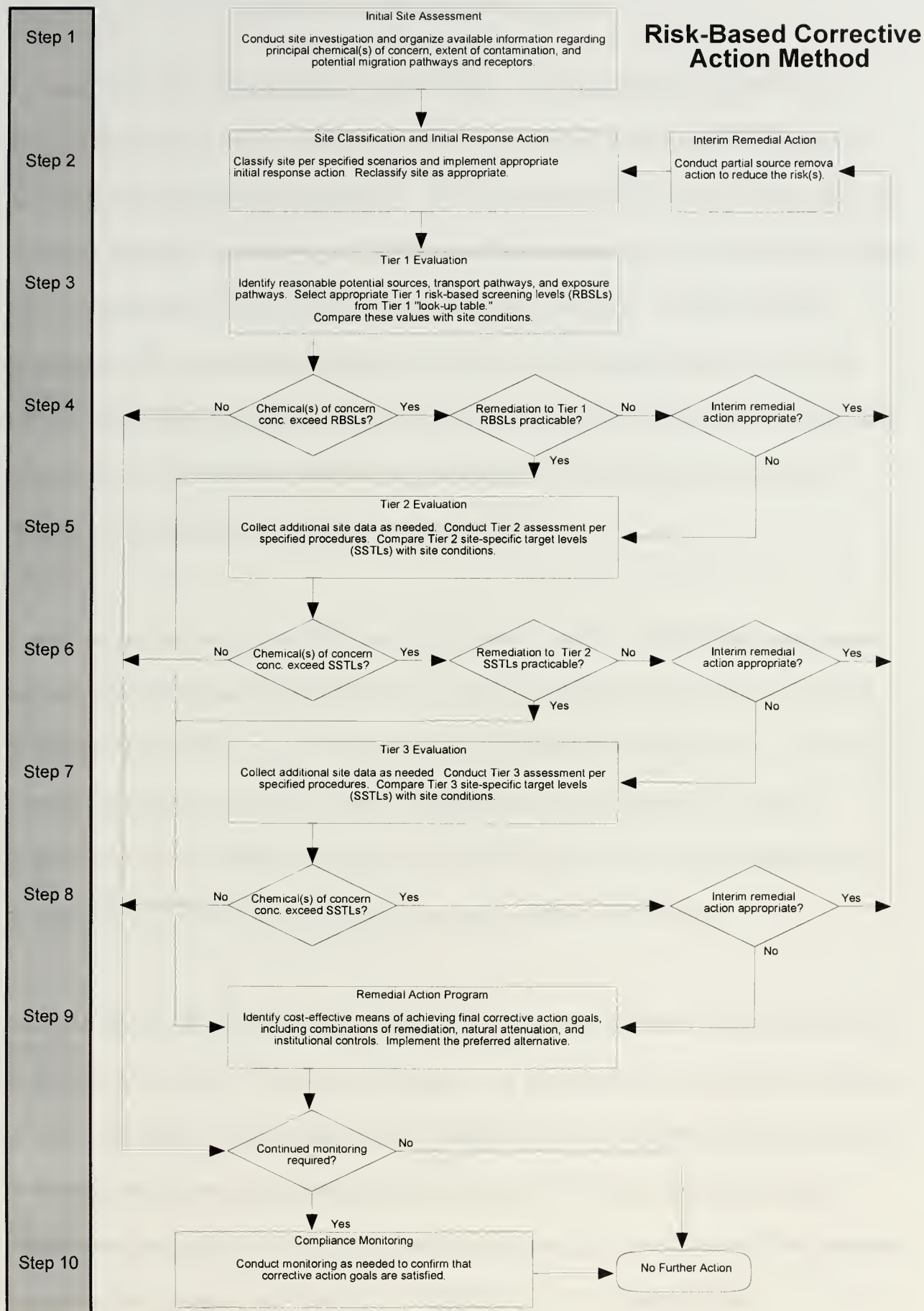


Figure 1: Begley, p. 440A.

The table of RBSLs can be related to federal, state, or locally-determined acceptable risk levels. Consequently, states, even if they agree to a consistent, nationwide RBCA method, can still develop the RBSLs independently. This so long as the RBSLs, as they are named, are *risk*-based and not just arbitrary, generic figures. These screening levels are used to determine appropriate responses, including the need for additional assessment. Concentrations of contaminants that pose immediate threats to receptors can be quickly remediated at any tier without undermining the process. As the decision tree illustrates, if none of the contaminants of concern exceed the RBSLs, then the process is complete except for a determination of whether or not to continue monitoring the affected site.

Tier II analysis and evaluation builds on the Tier I results and is tailored to the contaminants and pathways that exceed the Tier I RBSLs. Information gathered at this stage is also input into simple, conservative models to project the contaminant's fate and transport. Site-specific target levels (SSTLs) are evaluated along contaminant migration pathways at points of concern. Treatment variables such as the current and future land use and the disposition of groundwater are factored into the choice of possible responses at this level.

Tier III concerns specific site conditions and is used when Tier II SSTLs cannot be met or the simple fate and transport models are inappropriate. A technically more sophisticated analysis should be performed which includes complex chemical fate and transport models and statistical probability evaluations of possible exposures and risks. The Tier III evaluation can be compared to the detailed level of risk assessment conducted for Comprehensive Environmental Response, Compensation and Liability Act (CERCLA, a.k.a., Superfund) sites.

The impetus for California's move to a modified RBCA standard is the UST program. The underground storage tank program in California has been in existence since 1984 when findings that a significant percentage of underground storage tanks leaked prompted State legislation to address the problem. The vast majority of underground tanks contain petroleum products, mainly gasoline. The typical procedure currently followed after identifying a petroleum release is to repair or remove the tank to stop the leakage, define the volume of affected soils and/or groundwater through soil borings and groundwater monitoring wells, and actively remediate the affected volumes of soil and groundwater.

Because of the numbers of leaking or suspect tanks, the Underground Storage Tank Program of the California State Water Resources Control Board contracted with the Lawrence Livermore National Laboratory (LLNL) to review the current regulatory framework and cleanup process. The results of the review were released on October 16, 1995, in a report titled "Recommendations to Improve the Cleanup Process for California's Leaking Underground Fuel Tanks (LUFTs)".

II. A. Summary of the LLNL Report¹²

II. A. 1. Findings/Conclusions

1. LUFT Impacts to Groundwater Resources-

Among 12,151 public water supply wells tested statewide, only 48 (0.4%) had benzene concentrations above the analytical detection limits. Additionally, a review of California's LUFT cases (totaling 28,051 statewide) demonstrated that only 136 LUFT sites (0.5%) have affected drinking water wells. In general, the affected wells were private, domestic wells sunk

in shallow aquifers near a LUFT release site.

2. Derivation of LUFT Cleanup Requirements-

Under current regulations and policies, the minimum cleanup standards for LUFT cases affecting groundwater are the Maximum Contaminant Levels (MCLs) for drinking water. One of the reasons for this is the application of the State Board's Resolution 88-63 (Sources of Drinking Water Policy) which requires almost all state waters to be designated as potential sources of drinking water. Strict cleanup is also indicated by the existing version of the state's groundwater cleanup policy (Resolution 92-49) which sets background water quality as a cleanup goal. Numeric cleanup standards are not established for residual fuel hydrocarbons in soils.

3. Application of LUFT Regulatory Framework-

Groundwater cleanup requirements were found to be consistently applied statewide, due to the presence of numeric standards. As a practical matter regional boards and local agencies usually rely on the MCL limits for benzene (1 ppb), toluene (100 ppb), ethylbenzene (680 ppb), and xylenes (1,750 ppb) as cleanup levels instead of insisting on cleanup levels to actual background levels or to odor and taste thresholds. Many cases are difficult to close because achieving the existing groundwater standards and goals is often technically and economically infeasible.

4. Technical Feasibility-

The report observes that, if a fuel hydrocarbon source is removed, passive bioremediation

processes act to naturally reduce the fuel hydrocarbon plume mass and eventually complete the fuel hydrocarbon cleanup. Passive bioremediation can provide a remediation alternative that is as efficient as actively engineered remediation processes such as pump and treat.

5. Economic Impact of Current LUFT Problem-

The average LUFT case reimbursement from the Underground Tank Cleanup Fund is currently about \$150,000. The number of tank removals is expected to increase dramatically in the next few years, due to the requirements of federal regulations and state law requiring all operating USTs to be upgraded or replaced by 1998. The majority of UST releases are discovered when the tanks are removed and leakage from piping is uncovered. The ongoing and future fiscal effect of LUFT cleanups on the California economy is estimated to be over \$3 billion. Only about \$1.5 billion will be raised by the time the Cleanup Fund program ends in 2005.

II. A. 2. Recommendations

The primary recommendations of the report follow were (1) that passive bioremediation should be considered as a remediation alternative whenever possible; (2) that State Board policies should be modified to allow risk-based decision making for LUFT cleanups; and, (3) that such risk-based cleanups should use passive bioremediation whenever possible. In their report, the authors also outlined the factors that the Regional Water Quality Control Boards (RWQCBs) should consider to determine when passive bioremediation might be appropriate. Both Section III and Appendix A of this paper will outline the specifics in greater detail.

II. B. Public/Agency Response to the LLNL Report

II. B. 1. California State Water Resources Control Board (SWRCB)

Following the release of the Lawrence Livermore Report, Mr. Walt Pettit, Executive Director of the State Water Resources Control Board, issued "Interim" guidance from the State Board on December 8, 1995 concerning the implementation of the findings of the report. In this memo, Mr. Pettit outlined the two most significant points raised by the LLNL report. He called attention to (1) the finding that the impacts to the environment from leaking USTs were not as significant as once believed; and (2) the follow-on recommendation that "passive bioremediation should be considered as the primary remediation tool in most cases once the fuel leak source has been removed."¹³ Mr. Pettit further recommended that cleanup oversight agencies eliminate the requirement for active remediation at low-risk soil and groundwater cases. Specifically, he suggested that low-risk soil cases be closed and, in the case of low-risk groundwater cases, that the Regional Boards transition from active remediation to monitoring. However, a clear definition of what constitutes a "low-risk" case was not included in the letter. Subsequently, discussions with the State Board's Underground Tank Program Manager, Mr. James Gianopoulos, provided direction that the individual Regional Boards could, in keeping with their specific regional settings, determine how to define low-risk cases.

II. B. 2. Santa Ana Regional Water Quality Control Board Staff's Response

While the State Board has embraced the LLNL report, the reactions of other regulatory agencies were mixed. Within the Santa Ana Region, a high level of urbanization, a high and increasing dependence on water supply derived from groundwater and a relatively transmissive aquifer setting combine to create a situation where the groundwater resources are highly

valued and susceptible to contamination. As a result, the Santa Ana Regional Board has taken a much more conservative view of the LLNL report and is not anxious to move to a modified RBCA framework.

In addition, Staff's review of the details of numerous groundwater cases within the Santa Ana Region suggested that not all of the findings of the LLNL report are supported by the data within their particular case files. The most noteworthy observation is that a significant percentage of the Santa Ana RWQCB's groundwater cases are more than ten years old yet still exhibit elevated concentrations of benzene. This observation is in contrast to the LLNL report's assertion that petroleum compounds in groundwater rapidly degrade.

Skepticism, like that exhibited by the Santa Ana Regional Board, is a predictable reaction to any regulatory change. Regulatory agencies have traditionally held very conservative institutional views. Arguably, they have a tremendous responsibility to protect human health and the environment and must consider public perception. Environmental educators and research scientists need to continue to offer scientifically based assurances that strengthen resolve toward the most appropriate actions, including change from more to less conservative environmental regulation that in no way compromises the basic tenet of protection. These scientifically based assurances might be offered by additional empirical data to support the estimates of current fate and transport models or new toxicity studies on whole petroleum compounds.

II. B. 3. Distrust

There are those that are distrustful of RBCA because they fear the potential to “calculate away” risks to human health and the environment. Certainly, there are cases where remediation will be necessary, cases where “calculating away” the risk is inappropriate if not negligent. This is particularly true in instances where unsuitable soil conditions or complex contaminant mixtures are present. Because the RBCA decision framework is highly dependent upon the scientific measurements and an accurate site assessment, declining to remediate on the basis of questionable data is irresponsible. Where the data exists, however, it would be *fiscally* irresponsible not to apply RBCA. Federal and state monies, as well as the assets of private entities, should be spent as efficiently as possible to reduce potential threats to human health and the environment.

In fact, where there are human or ecological receptors, the remediation requirements dictated at the conclusion of the RBCA decision making process are just as strict as they are for any other environmental corrective action. In order to overcome the public distrust employing RBCA as a new policy, environmentalists and regulators will need to emphasize this point repeatedly.

II. C. DoD Petroleum Hydrocarbon Cleanup Demonstration Program

The objective of the demonstration program is to field test and refine the California modified risk-based corrective action protocol (CalRBCA) being developed by the State Water Resources Control Board in cooperation with U. S. EPA and the Department of Defense (DoD).

Like the ASTM standard, CalRBCA will be a tiered risk-based decision making process for petroleum hydrocarbon contaminated sites. The purpose of this systematic approach is to avoid unwarranted site remediation expenses, analysis or delays, while ensuring adequate site characterization to identify the extent of contamination or design appropriate responses to a contamination problem.

The four active Defense forces all have bases in California in various geographic and diverse hydrogeologic settings. To support the study, one or two former tank sites from 7 of the state's 9 Regional Water Quality Control Boards, was chosen to apply CalRBCA. Two Regional Water Boards, Regions 1 and 7, do not have demonstration sites within their region and will participate with a neighboring Board. Each of the services is represented and the sites vary in complexity from soil contamination only to soil and groundwater contamination coupled with free product perched on the water table.

The intent of the demonstration project, in addition to providing the agencies a “training ground” for CalRBCA, is also to get regulatory and public acceptance for this approach. It may also help demonstrate sampling and monitoring procedures to support intrinsic bioremediation.

The demonstration project is still in its infancy. At Marine Corps Air Station (MCAS) El Toro, the Pilot Study scoping meeting was held in July 1996 to kick off the process. A second meeting to brief the Expert Committee and present the results of site assessment sampling and analysis was held in January 1997.

II. D. MCAS El Toro

II. D. 1. Background

Marine Corps Air Station (MCAS) El Toro was established in 1942 as an operational training facility for Marine Corps pilots. In support of that function the base has provided and maintained facilities for both aviation and ground support activities including aircraft maintenance, flight line operations, and administrative areas. MCAS El Toro is now planning for the closure and disposal of the base by July 1999 in accordance with the Base Closure and Realignment Act of 1993.

Prior to base closure in July 1999, MCAS El Toro must close or at least initiate closure action for its 408 UST sites. To date, of the 408 USTs, only 57 are still active and 282 have been removed. Of the 282 removed tanks, 221 have received letters documenting regulatory closure by the local Orange County Health Care Agency (OCHCA) or the Regional Water Quality Control Board. (The closure agency depends upon whether or not the site required remediation prior to closure. The OCHCA closes sites with clean removals while the RWQCB evaluates former sites after remediation and confirmation sampling.)

Among the former tank sites that are not closed, several have demonstrated significant petroleum hydrocarbon contamination in soil and one has significantly impacted groundwater. Because the predominant media affected at MCAS El Toro is soil and the groundwater site is undergoing active remediation including free product removal, I will focus my discussion on our soil sites. Two sites collocated with one another, former USTs 390A & B were selected for the CalRBCA DoD Demonstration Project.

II. D. 2. Environmental Setting

The base is located within central Orange County, California, approximately 45 miles southeast of Los Angeles. It occupies approximately 4,738 acres, with about 800 of those acres designated for agricultural outleases. Geologically, the base is located on the southeastern edge of the Tustin Plain and lies above sediments derived mainly from the Santa Ana Mountains. The sediments consist of isolated, coarse-grained, stream channel deposits contained within a matrix of fine-grained overbank deposits. They are poorly sorted and are generally heterogeneous with interbedded lenses of fine-grained clay to coarse gravel stringers. The sediments have moderate to high porosity and permeability.¹⁴

Approximately 180 groundwater monitoring wells were constructed during the remedial investigation of 25 CERCLA sites aboard base. They demonstrate that the regional groundwater gradient for the shallow aquifer is generally northwest to west-northwest. The shallow aquifer is also deep in this area, averaging 100 to 200 feet below ground surface (bgs) for much of the base.¹⁵

The local climate is characterized by low average annual rainfall. The rainy season is primarily November through March, averaging 12.2 inches per year. Summer temperatures rarely exceed 100°F and winter temperatures seldom drop below freezing.

II. D. 3. Site Characterization, Site 390

Information maintained by the base with respect to underground storage tanks was somewhat spotty prior to 1985. With the advent of new regulations and a higher public interest, better

records were established. In any case, prior to 1985, the base only maintained property records for its large plant property, namely buildings. The property cards generally listed the significant features of a facility when it was constructed including such equipment as underground storage tanks, however, the property records did not generally record inactivation of USTs unless it was coincident with building demolition. Therefore, while we have good records of UST installation dates, their inactivation cannot be reliably pinpointed. Such was the case with Site 390. The site was comprised of two USTs, 390A & B, a dispenser island, and piping.

These two single-wall, steel tanks were installed in 1955 and removed in July 1993. While we know that the system was abandoned sometime prior to the tank removal, we cannot determine the exact date or even year. Correspondence with the Orange County Health Care Agency (OCHCA) confirms that the tanks were definitely abandoned prior to March 1991 and the station's best estimate is that they were abandoned sometime before 1989. Both tanks reportedly held fuel oil although there is some evidence that one or both of the tanks held gasoline at some point during its active years. UST 390A was a 500 gallon tank while 390B had a 2,000 gallon capacity.

Risk analysis for most MCAS El Toro former UST sites is simplified by the absence of ecological receptors in the vicinity of the former leaking tanks. Receptor identification for the potential future use scenarios was based upon several premises. First, given that the ultimate reuse for the base has not been finalized by the County of Orange, the local reuse agency (LRA), we need to conduct risk-assessment for both a future industrial/commercial scenario

and a future residential scenario. At this point, based upon the LRA's preferred alternative, MCAS El Toro will become a commercial international airport. Of course, the most conservative scenario for future reuse is a residential setting that presupposes that the asphalt paving currently covering former UST site 390 will be removed. This scenario is also the only one with a child as the receptor and, consequently, uses even more conservative figures, including a higher soil ingestion rate and lower body weight.

Additional assumptions that are also noted in the Site Conceptual Exposure Scenarios in appendix A, are that construction workers will be exposed to soil up to 10 feet below ground surface. We will use the highest measured contaminated soil concentration between 0 and 15 feet bgs to conservatively assess risk to construction workers. The scenario involving on-site industrial or commercial workers, both current and future, presumes that the asphalt paving currently in place will remain, thereby removing any direct pathways to soil and removing the secondary source of airborne contaminated soil particulates.

III. Natural Attenuation

Natural attenuation of contaminants in soil and groundwater, often called intrinsic remediation, is the result of a number of natural fate and transport mechanisms including biodegradation, chemical or abiotic reactions, diffusion, sorption, dilution, volatilization, dispersion, and advection. Engineered solutions to contamination problems also use one or more of the natural fate and transport mechanisms but generally take less time (through the introduction of energy, nutrients, or other engineering controls) and cost significantly more money. 1993 estimates for facilitated *in situ* bioremediation, for example, ranged from \$30 to \$100 per

cubic yard with treatment periods from six months to several years (depending upon soil concentrations, cleanup criteria and type of petroleum product).¹⁶

Natural attenuation has worked successfully at a number of sites. In 1994, Kampbell, Wiedemeier and Hansen¹⁷ characterized a 700 gallon gasoline spill that occurred in 1986 at an automobile service station in Cocoa Beach, Florida. They looked at site-specific data to demonstrate that natural attenuation was successful and that the contaminated groundwater had sufficient capacity to degrade all dissolved BTEX within 250 meters down gradient of the spill. The three separate lines of evidence were a reduction or loss of contaminants on a field scale, geochemical data, and the presence of intermediate microbial BTEX breakdown products. The contaminants of concern and, consequently the group's indicator chemicals were BTEX.

After Kampbell *et al.* demonstrated contaminant loss on a field scale, they evaluated the groundwater chemistry to determine the relative importance of the significant operating natural attenuation mechanisms. Measured parameters included redox potential; water temperature; dissolved oxygen, ferrous iron, methane, nitrate and sulfate concentrations; pH; and alkalinity. A warm water temperature of 26°C and pHs near 7 suggested near optimal conditions for microbial degradation. Moreover, total alkalinity ranged from 148 to 520 mg/l which was sufficient to ensure buffering of pH changes during microbial reactions. The redox potential measured between 54 to -293 mV with the low redox potential readings coinciding with low dissolved oxygen, higher BTEX and methane concentrations. The results of their measurements indicated that BTEX reduction was primarily due to aerobic respiration, iron

reduction and methanogenesis.

Finally, the group performed an analysis on the groundwater for phenols and aliphatic/aromatic acids. The presence of these fatty acids, intermediate products of biodegradation, further supported that natural attenuation, primarily by microbial biodegradation, was functional and viable.

Closer to MCAS El Toro, Henry and Hansen¹⁸ evaluated a site within the greater Los Angeles basin. Again the contamination was gasoline at an automotive service station. In this case, at least one of three former 8,000 gallon USTs had leaked an indeterminate amount of gasoline prior to their replacement by double-walled tanks. During the tanks' removal, analysis indicated up to 7,200 mg/kg TPH-gasoline in the soil at a sampling depth of 14 feet. Because the concentration exceeded the local agency's regulatory action threshold, the site was actively remediated by removal of the contaminated soil to the extent practical. The practical limit of the excavation proved to be about 20 feet bgs. Additional soil sampling after excavation still indicated TPH-gasoline concentrations in the soil of 1,000 to 3,000 ppm. Excavation was halted and all parties pursued site characterization to determine whether or not natural attenuation was a feasible alternative in this case.

Characterization included identifying depth to groundwater (greater than 100 feet bgs), soil types (sandy silts, silty sands, sand and gravel), and extent of contamination. The results demonstrated that contamination had not spread laterally and had only affected soil to a depth of approximately 30 feet bgs, just 10 feet below the limits of the excavation. Henry and

Hansen then took a completely different approach to that of Kampbell *et al.* to demonstrate the viability of natural attenuation.

They began by estimating the residual saturation of the gasoline. The foundation for this line of reasoning was that the downward migration of the gasoline took place because there was enough liquid present for flow in the unsaturated soil. However, as the liquid moved downward through the soil, a small amount would attach itself, or adsorb, to the soil particles in its path. Ultimately, because of the large volume of unsaturated soil and the relatively small mass of remaining contaminant, the leaked gasoline will become adsorbed to the soil until the degree to which it saturates the soil reaches a point called “residual” saturation. At that point the downward migration of the gasoline is essentially halted.

The two primary factors which influence the volume of soil necessary to immobilize a finite amount of product are the porosity of the soil and the characteristics of the hydrocarbon measured as its “maximum residual saturation”. The residual saturation for various hydrocarbon products has been empirically derived and approximated as 10% for gasoline, 15% for diesel and light fuel oil, and 20% for lube and heavy fuel oil.¹⁹ Using those residual saturation percentages, Henry and Hansen calculated theoretical hydrocarbon concentrations required for residual saturation using soil porosities ranging from 20 to 60 percent. They used the following formulae to calculate the range of concentrations shown in Table 1:

$$(1) \quad C_h = W_h / (W_h + W_s) \quad \text{where } C_h \text{ is the hydrocarbon concentration}$$

W_h is the hydrocarbon weight
 W_s is the soil weight = 146 lb/ft

(2) $W_h = W_w \times \sigma_g \times RS \times \eta$ where W_w is the unit weight of water = 62.4 lb/ft
 σ_g is the specific gravity of gasoline = 0.80
 RS is the residual saturation = 0.10
 η is the porosity, varies from 0.20 to 0.60

Table 1: Theoretical Residual Hydrocarbon Concentration (mg/kg)

Soil Porosity (%)	Residual Saturation (% of total)					
	5	10	15	20	25	30
20	3,400	6,800	10,200	13,600	17,000	20,400
30	5,100	10,200	15,300	20,400	25,400	30,500
40	6,800	13,500	20,300	27,000	33,800	40,500
50	8,512	17,024	25,536	34,304	42,560	51,072
60	10,144	20,288	30,432	40,576	50,720	60,864

Source: Henry and Hansen (1993), p. 506.

From the above table, the residual hydrocarbon concentration in the soil ranges from 3,400 to 60,864 mg/kg. At a minimum then, the soil hydrocarbon concentration would have to exceed at least 3,400 mg/kg (the most conservative figure) for the gasoline to move as a liquid in the soil. Since the maximum concentration measured during site characterization was 3,000 mg/kg the authors concluded that leaving the contaminated soil in place would not pose a threat to groundwater. Since the contaminated soil posed no current or reasonably foreseeable future threat, natural attenuation of the soil media was deemed appropriate.

III. A. “Nondestructive”/Physical Transport Mechanisms

There are a number of physical transport mechanisms that influence the nature of a cleanup site. Generally, these mechanisms reduce the concentration of the contaminant at the original spill or leak location but tend to spread the contamination over a larger volume and into other phases. These transport mechanisms do nothing to actually reduce the mass of the contaminant. Also, while I outline these physical transport processes here, keep in mind that

transport in the subsurface environment (soil and groundwater) is generally very slow compared to surface water or air transport.

Advection is the bulk movement of a contaminant with its carrying medium. This strict definition implies no effect on the contaminant's concentration in the medium, the best comparison would be strict plug flow in a pipe. This transport mechanism is influential with surface and groundwater contamination and also has implications when designing pump-and-treat groundwater or soil vapor remediation systems. It is a three dimensional process, but to simplify, advection in one direction can be quantitatively described by:

$$M_x = Q_x \times C_f$$

where M_x = mass of chemical transported by advection
in the x-direction [mass/time]
 Q_x = volumetric flow rate of the fluid in the x-
direction [volume/time]
 C_f = concentration of the chemical in the fluid
[mass/volume]

There are two predominate types of diffusion, molecular diffusion results from the random movement of the molecules. The contaminant eventually moves from an area of high concentration to areas of lower concentration. Since it relies on molecular motion it is a very slow process relative to other transport mechanisms. In fact, where advection is present, this mechanism is insignificant. It should be considered, however, when the fuel contamination in soil moves to the soil vapor phase. In these cases it can be quantified using Fick's Law.²⁰

Mechanical dispersion is the result of velocity variations that are not captured by advection. It only occurs in the presence of bulk movement. In the subsurface environment, mixing is not the result of turbulence but instead is caused by water moving through porous media and

encountering obstacles that reroute its flow. Dispersion is a three dimensional transport mechanism that is difficult to measure. It can be approximated using empirically derived dispersivity coefficients in literature as followed²¹:

$$M_{dx} = -D_x \frac{\delta C}{\delta x} A_x$$

where M_{dx} = mass of chemical transported due to mechanical dispersion in the x-direction [mass/time]
 D_x = effective mechanical dispersion coefficient in the x-direction [area/time]
 $\delta C / \delta x$ = concentration gradient in the x-direction
 A_x = the cross-sectional area in the x-direction

The mechanism of adsorption is generally considered a chemical as opposed to a physical phenomenon. It describes the degree to which a chemical “sticks” to the surface of a solid. I have grouped it here, however, because like the physical processes, chemical sorption does not reduce the total contaminant mass. Adsorption, like physical transport, is a “nondestructive” mechanism.²² Unlike the physical transport processes, however, adsorption does not speed the transport of the contaminant, it typically reduces contaminant mobility, that is, *retards* it. Adsorption depends on both the contaminant and soil characteristics and, consequently, is either empirically derived or estimated using isotherms. In general, hydrophobic compounds tend to adsorb onto solid organic materials.

III. B. Physical Properties affecting transport

Specific density is the density of a substance divided by the density of pure water at standard temperature and pressure. The density of petroleum products is important for non-aqueous phase liquids (NAPLs) migrating through the unsaturated soil zone and reaching groundwater. Generally, liquids that are less dense than water, that is, with specific gravities less than 1.0, tend to float on the groundwater table. As a result, these lighter NAPLs tend to migrate in

groundwater along the general direction of flow. In contrast, dense NAPLs, with specific gravities greater than 1.0, will sink and do not necessarily follow the groundwater flow.

While the individual compounds have varying specific densities, with the BTEX compounds being lighter than water and the polycyclic aromatic hydrocarbons (PAHs) being heavier, their individual densities are not as relevant as the petroleum hydrocarbon compound itself. Nearly all hydrocarbon products are less dense than water.²³

The most significant property affecting groundwater contamination by petroleum products is solubility. Solubility is qualitatively defined as the mass of a chemical that will dissolve in a unit volume of water. It is a function of temperature, pressure, pH, and the concentration of other dissolved components of the solution. In general, the lighter aromatics, i.e. BTEX, are highly soluble, with measured solubilities ranging from 152 mg/l for ethylbenzene to 1780 mg/l for benzene at 20°C.^{24, 25} The solubility of the petroleum component will impact its concentration in both soil moisture and groundwater.

Finally, a compound's volatility describes the degree to which it tends to partition between its liquid and gaseous phases. In the subsurface environment this physical property of a compound is less influential than solubility. However, in the vadose or unsaturated soil zone, chemicals can (and do) volatilize into soil gas. Near the surface, these soil gases can escape and become a source of indoor air contamination or be transported through the outdoor air where they are quickly dispersed.

III. C. Biochemical transformation

The emphasis of any remediation process or design should be on fate (transformation) mechanisms versus transport mechanisms. The transport processes do not reduce the overall contaminant mass but rather spread it out over a larger volume of the phase or simply move it from one media to another, from the soil to water, soil to air, etc. Moreover, among the transformation processes, the emphasis should be on biotransformation. While inorganic degradation of hydrocarbon compounds is possible, microbial degradation reactions result in much faster degradation *rates* than inorganic transformations.²⁶

One cannot discuss the advantages of RBCA without at least a brief discussion of intrinsic bioremediation. The discussion also has merit because, to those that oppose using natural attenuation as a "cleanup process", it is a logical conclusion that any biodegradation process that occurs naturally in the environment can also be applied in a variety of engineered settings such as land biotreatment facilities, thermal desorption units, and groundwater pump and treat systems. Likewise, biodegradation can be facilitated *in situ*, with the introduction of engineering controls.

In many instances, fuel hydrocarbon remediation is best left to nature given the cost and inefficiency of active remediation technology. LLNL concluded that passive bioremediation can be as efficient, if not more so, than proactive remediation technology. In effect, the vadose zone and aquifer act as a large *in-situ* bioreactors for degrading the organic contaminants in the soil and groundwater.²⁷ US EPA supports passive bioremediation as good science but opts to consider the process an "active remediation technology." EPA

recommends a combination of aggressive characterization with passive bioremediation.

The most significant fate mechanism is biochemical transformation, also referred to as biodegradation or bioremediation.²⁸ To be technically accurate, biodegradation is the general term used to describe the cumulative effects of numerous biotransformation steps. Ultimately, this mechanism transforms the organic compounds such as petroleum hydrocarbons and BTEX to innocuous inorganic compounds such as carbon dioxide (CO₂) and water through a wide variety of processes. The terminal degradation to CO₂ and water is also called mineralization. As an example, benzene biodegradation can occur through aerobic respiration, denitrification, iron reduction, sulfate reduction, and methanogenesis.²⁹ These reactions are represented as follows:

Figure 2: Benzene biodegradation reactions

Aerobic respiration	$7.5\text{O}_2 + \text{C}_6\text{H}_6 \rightarrow 6\text{CO}_2 + 3\text{H}_2\text{O}$
Denitrification	$6\text{NO}_3^- + 6\text{H}^+ + \text{C}_6\text{H}_6 \rightarrow 6\text{CO}_2 + 6\text{H}_2\text{O} + 3\text{N}_2$
Iron reduction	$6\text{OH}^+ + 3\text{OFe}(\text{OH})_3 + \text{C}_6\text{H}_6 \rightarrow 6\text{CO}_2 + 3\text{OFe}^{2+} + 78\text{H}_2\text{O}$
Sulfate reduction	$7.5\text{H}^+ + 3.75\text{SO}_4^{2-} + \text{C}_6\text{H}_6 \rightarrow 6\text{CO}_2 + 3.75\text{H}_2\text{S} + 3\text{H}_2\text{O}$
Methanogenesis	$4.5\text{H}_2\text{O} + \text{C}_6\text{H}_6 \rightarrow 2.25\text{CO}_2 + 3.75\text{CH}_4$

Source: Kampbell *et al.* (1996), p. 198.

Bioremediation usually takes place by oxidation of petroleum hydrocarbons and involves transfer of electrons from an electron donor to an electron receptor. In the case of petroleum degradation, the fuel hydrocarbons serve as the electron donors, or carbon sources for the microorganisms. Aerobic microbes use dissolved oxygen as the electron acceptor, whereas anaerobic microbes use electron acceptors such as nitrates, iron (III), sulfate, and carbon

dioxide. For fuel hydrocarbons the degradation rate under anaerobic conditions is slower than under aerobic conditions. However, in a typical plume anaerobic conditions exist over a larger area, and consequently, a significant reduction in the total contaminant mass can be attributed to anaerobic biodegradation.³⁰ At these sites the absence of or low concentrations of dissolved oxygen (DO) in the impacted groundwater plume indicate that intrinsic bioremediation is taking place.

The effectiveness of intrinsic bioremediation is site specific and depends upon the contaminants and the hydrogeologic setting. A thorough assessment of its potential effectiveness must be conducted prior to implementation. Many of the necessary steps for this assessment are already performed during the site assessment step of the RBCA process.

The assessment is necessary to estimate the time required to achieve cleanup goals, confirm that throughout this period the contaminants will not impact a receptor, and that protection of human health and the environment will not be compromised. The assessment may also assist in developing a long term monitoring plan consistent with local regulations. In some instances, the available site data is incomplete and while it may not support a RBCA decision of “no further action”, it can be used in existing fate and transport models to estimate the effectiveness of intrinsic bioremediation or to design engineered bioremediation systems.

The intrinsic bioremediation process has been known to exist for a long time, however, the recent emphasis on RBCA and a better understanding of the underlying mechanisms have brought this technology to the forefront. Unlike most other natural attenuation processes

intrinsic bioremediation causes an actual reduction in the contaminant mass, and the contaminants are not merely transferred from one media to another.

III. C. 1. Petroleum-degrading microbial population

Many distinct studies of biological remediation have concluded that ubiquitous microorganisms have the ability to degrade, by biotransformation, fuel hydrocarbons in soil and water. The two biggest players in this biodegradation processes are bacteria and fungi although the relative importance of each is undetermined.³¹

Table 2. Genera of Hydrocarbon-Degrading Bacteria and Fungi Isolated from Soil

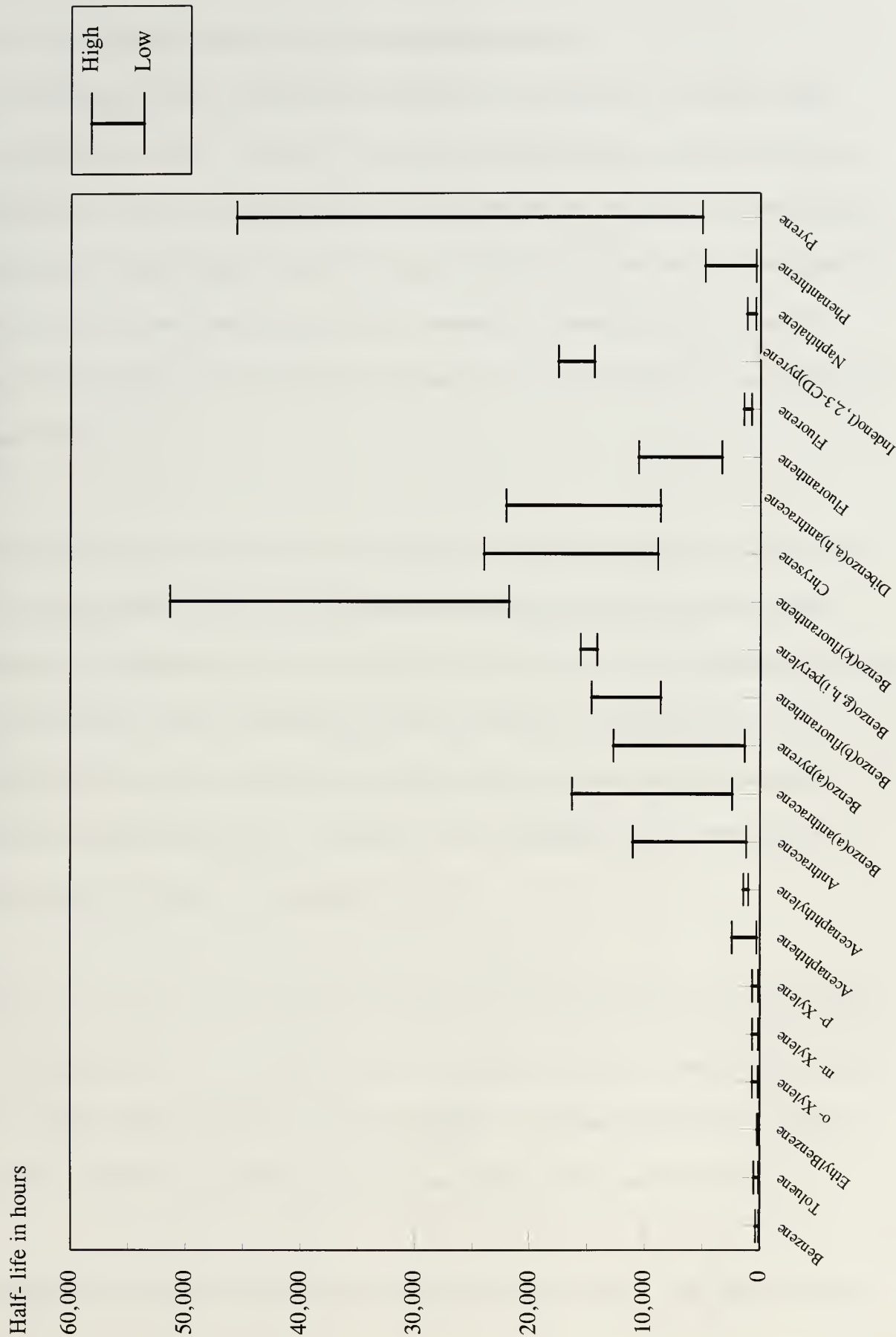
Bacteria	Fungi
<i>Achromobacter</i>	<i>Acremonium</i>
<i>Acinetobacter</i>	<i>Aspergillus</i>
<i>Alcaligenes</i>	<i>Aureobasidium</i>
<i>Arthrobacter</i>	<i>Beauveria</i>
<i>Bacillus</i>	<i>Botrytis</i>
<i>Brevibacterium</i>	<i>Candida</i>
<i>Chromobacterium</i>	<i>Chrysosporium</i>
<i>Corynebacterium</i>	<i>Cladosporium</i>
<i>Cytophaga</i>	<i>Cochliobolus</i>
<i>Erwinia</i>	<i>Cylindrocarpon</i>
<i>Flavobacterium</i>	<i>Debaryomyces</i>
<i>Mircococcus</i>	<i>Fusarium</i>
<i>Mycobacterium</i>	<i>Geotrichum</i>
<i>Nocardia</i>	<i>Gliocladium</i>
<i>Proteus</i>	<i>Graphium</i>
<i>Pseudomonas</i>	<i>Humicola</i>
<i>Sarcina</i>	<i>Monilia</i>
<i>Serratia</i>	<i>Mortierella</i>
<i>Spirillum</i>	<i>Paecilomyces</i>
<i>Streptomyces</i>	<i>Penicillium</i>
<i>Vibrio</i>	<i>Phoma</i>
<i>Xanthomonas</i>	<i>Rhodotorula</i>
	<i>Saccharomyces</i>
	<i>Scolecobasidium</i>
	<i>Sporobolomyces</i>
	<i>Sprotrichum</i>
	<i>Spicaria</i>
	<i>Tolypocladium</i>
	<i>Torulopsis</i>
	<i>Trichoderma</i>
	<i>Verticillium</i>

Source: Englert *et al.* (1993), p. 113.

Table 2, excerpted from Englert *et al.*, lists the genera of hydrocarbon-degrading bacteria and fungi isolated from soil. “In decreasing order, *Pseudomonas*, *Arthrobacter*, *Alcaligenes*, *Corynetacterium*, *Flavobacterium*, *Achromobacter*, *Micrococcus*, *Nocardia*, and *Mycobacterium* appear to be the most consistently isolated hydrocarbon-degrading bacteria from soil.”³²

Numerous empirical studies have been conducted to determine the biodegradation rate of various compounds. The rate is best described in terms of half-life, the amount of time it takes to biodegrade the contaminant to half of its initial mass.³³ The BTEX compounds generally have much shorter half-lives than the more persistent PAH compounds. Figure 3 illustrates the reported range of experimental and field tested biodegradation rates of BTEX and PAH compounds in soil.

Figure3: Reported Range of Empirical Biodegradation Rates



Source: Metcalf & Eddy (1993), p. 4-10.

III. C. 2. Soil and water factors affecting biodegradation

The most significant factor affecting biodegradation is the availability of suitable energy sources for the microbes. Absence or scarcity of an available energy source limits growth. Fortunately, most of the petroleum hydrocarbon-degrading microorganisms are heterotrophic and use the available organic carbon for energy.³⁴ In fact, in the presence of hydrocarbons in soil, microbial growth and activity increases, although the diversity of aerobic microbial species is diminished. Fuel hydrocarbon contamination had little effect upon anaerobes in the same studies.³⁵

Arguably, for groundwater systems the availability of dissolved oxygen (DO) is the second most important factor. While biodegradation can occur either in the presence of oxygen (aerobic) or its absence (anaerobic), for petroleum hydrocarbons aerobic degradation can occur at rates up to two orders of magnitude faster than anaerobic biodegradation rates.³⁶ In a petroleum hydrocarbon-contaminated groundwater plume, both aerobic and anaerobic conditions exist at the same time. Generally, in the unsaturated zone for subsurface soil contamination, oxygen is not as influential a factor.

Thirdly, pH is a factor widely discussed in the literature because the pH affects the solubility of certain components. By elevating the pH, metals which adversely affect microbes become less soluble. While the literature varies moderately, the optimum pH for biodegradation of petroleum products is estimated to be in the range slightly above neutral to pH 8.^{37,38}

Temperature also affects biodegradation of petroleum hydrocarbons. This, like most other

biochemical reactions follows the general premise that the rate of the transformation reaction increases as temperature increases. There is, of course, a range where this general rule holds true but it is bounded by upper and lower limits particular to each type of microorganism. Many microorganisms contain essential enzymes that are denatured at temperatures of about 50°C , they also require liquid water for metabolism, therefore optimum aerobic degradation rates occur between 15°C and 50°C.³⁹

Finally, nutrients and other growth factors must be present for the biodegradation to occur. The principal inorganic nutrients needed for the microbial cell synthesis and growth are nitrogen, phosphorous, potassium, sulfur, magnesium, calcium, iron, sodium, and chlorine. Because the microbes, in the case of intrinsic bioremediation, need to derive all of these elements from their environment, a shortage of the appropriate ratio of any of these nutrients would limit growth. Nitrogen and phosphorous are the two nutrients most likely to be deficient in hydrocarbon impacted soil.⁴⁰ Typical values for the composition of bacterial cells are included in table 3.

Table 3. Typical Composition of Bacterial Cells

Percentage of dry mass			
Element	Range		Typical
Carbon	45 - 55		50
Oxygen	16 - 22		20
Nitrogen		12 - 16	14
Hydrogen		7 - 10	8
Phosphorous		2 - 5	3
Sulfur	0.8 - 1.5		1
Potassium		0.8 - 1.5	1
Sodium	0.5 - 2.0		1
Calcium		0.4 - 0.7	0.5
Magnesium		0.4 - 0.7	0.5
Chlorine		0.4 - 0.7	0.5
Iron	0.1 - 0.4		0.2
All others		0.2 - 0.5	0.3

Source: Metcalf & Eddy (1991), p. 365.

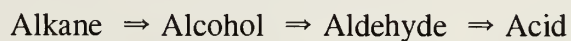
III. C. 3. Petroleum product chemical structure & its effect on biodegradation

The petroleum biodegradation process is complex and not fully understood yet. It is complicated by the high number of fuel additives and the wide variety of their makeup.

Additives consist of everything from de-icing agents to detergents to octane enhancers. Until specific research is conducted on each component, the potential degradability of petroleum hydrocarbons can be estimated given the chemicals comprising the petroleum product. I use generalities since there are hundreds of chemical components in gasoline or fuel oil.

Petroleum products are primarily comprised of varying combinations of three separate classes of hydrocarbons; alkanes, cycloalkanes and aromatics.

The alkanes (also called paraffins) are saturated hydrocarbons, meaning that all of the tetravalent carbon bonding sites not occupied by a single bond with another carbon atom are occupied, that is *saturated*, with hydrogen atoms. The normal alkanes (n-alkanes) are aliphatic or “straight-chain” hydrocarbons. All n-alkanes from C₁ to C₄₀ have been identified in petroleum products.⁴¹ Likewise, petroleum products contain isoalkanes, which have a branched chain structure, and cycloalkanes which have a saturated ring structure. These hydrocarbons, especially those with intermediate chain lengths (C₁₀ to C₂₄), degrade rather readily by a variety of bacteria and fungi. The biodegradation pathway can be summarized as follows:



The fatty acid is then metabolized through a beta oxidation pathway and the products of the degradation are ultimately carbon dioxide, water, and new microbial cells or biomass.⁴²

Aromatic hydrocarbons are unsaturated hydrocarbons consisting of rings of six carbon atoms. The simplest aromatic hydrocarbons consist of one ring. Among other chemicals, this group includes benzene (the simplest structure), toluene, ethylbenzene and xylenes, together abbreviated BTEX. BTEX is also degraded readily, although generally more slowly than the alkanes, through a variety of processes formerly summarized in Figure 2. The aromatic ring is cleaved to form a straight-chain acid. Depending upon the substituents of the ring the initial reactions may differ but molecular oxygen is typically used in one or more of the intermediate reactions.

An aromatic molecule can contain multiple carbon rings. This group of compounds are known as polycyclic aromatic hydrocarbons or PAHs, and represent the heavier molecular weight aromatic compounds. These compounds tend to demonstrate high adsorption characteristics and low solubility and, consequently, do not readily migrate through the soil to groundwater. Therefore they are generally degraded in the unsaturated soil zone. Their structure may also explain the slow biodegradation rates (expressed as half-life) in Figure 3.

Some of the complex hydrocarbons may be metabolized only slowly by microorganisms. In some cases, complete metabolism cannot be achieved without the aid of other microorganisms or alternate substrates to serve as additional carbon sources.

The authors of *The Elements of Bioenvironmental Engineering* conclude their discussion of hydrocarbon metabolism by reiterating a common belief among microbiologists that "...all naturally occurring compounds can be metabolized by microorganisms. Some can be

metabolized only if oxygen is available, some are metabolized only very slowly, and some only by a few species...” but they can be metabolized.⁴³

IV. Conclusion

IV. A. Maryland

In Maryland, the state regulators require analysis for total petroleum hydrocarbons (TPH) measured by EPA method 418.1, benzene, toluene, ethylbenzene, and xylenes (BTEX) using EPA methods 601/602, 624, or 625, and methyl tertiary butyl ether (MTBE) based on field screening.⁴⁴ A phone call to Mr. Mike Frank of the Maryland Department of Environment, Waste Management Administration, Oil Control Program, confirmed that Maryland is not among the states moving to RBCA but has adopted a “wait and see” attitude. Maryland may consider RBCA in the future depending upon the experience of other states. The State still uses TPH as its primary threshold parameter for UST remediation and has a fixed cleanup threshold of 100 ppm TPH for contaminated soil sites. Groundwater contamination must be remediated to below MCLs with 100 ppm total BTEX and 5 ppm benzene usually driving the cleanup decision threshold.⁴⁵ Mr. Frank also confirmed that Maryland currently tests for MTBE, and while it has not shown up at many tank sites, the State’s regulators expect the fuel additive to surface in future leaking tank sites.

IV. B. Over the horizon

Guidance from the EPA on when and how to implement natural attenuation for cleaning up petroleum and other contaminants is expected to be available soon. The guidance, entitled *Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground*

Storage Tank Sites, was originally expected to be ready for distribution in June 1997.

Currently under review at the regional offices, the EPA will address appropriate sites for natural attenuation, demonstration of the method through site characterization, performance monitoring, and contingency measures when monitoring shows that the method will not meet health and environmental protection goals.

One area that potentially should be studied further and, perhaps included as an aid to further decision making, would be a more formalized assessment of uncertainty in the overall RBCA model. Since uncertainties are an inherent part of toxicological data and inadequate mathematical models for complex chemical and biological processes, decisions might be aided by a formal assessment of uncertainty. The estimate of uncertainty's effect on the remediation decisions and estimates of the value of reducing the uncertainty could aid management or regulatory decisions in determining whether additional site assessment information is necessary before remediating or closing a given site.⁴⁶

Ultimately, the goal of an environmental engineer should be to design the most cost-effective, technologically feasible means of protecting human health and the environment. This is true whether researching the fate of pollutants to develop more environmentally responsible synthetic chemicals or designing a potable water treatment facility. I believe that the formal RBCA process is one effective way of accomplishing this goal by reducing the misallocation of resources and imposition of arbitrary, generic cleanup goals at low-risk sites. The limitations of RBCA are directly related to the technological shortcomings, our capability to model the fate and transport of pollutants, and the inherent flaws in current risk assessment models.

RBCA itself has not contributed to, nor solved these ills. It *does* provide a framework so that we can quickly evaluate and prioritize cleanup goals, and the framework itself does not need to change each time technological capability improves. We can then devote our time, attention and financial resources to more urgent, higher environmental risks and to advance our technological capabilities to remediate environmental pollutants.

Endnotes

- ¹ Rounds, Dennis D. and Paul C. Johnson. "Risk-Based Corrective Action at Petroleum Release Sites." *Standardization News*, **22**(5):p. 30, 1994.
- ² Stanley, Curtis C. and Paul C. Johnson. "Risk-Based Corrective Action." *Standardization News*, **24**(6):p. 22, 1996.
- ³ Bell, Charles E., Paul T. Kostecki, and Edward J. Calabrese. "Review of State Cleanup Levels for Hydrocarbon Contaminated Soils." In *Hydrocarbon Contaminated Soils and Groundwater*, eds. Paul T. Kostecki and Edward J. Calabrese. Chelsea, Mich: Lewis Publishers, 1991, p. 78.
- ⁴ Rapaport, Diane, and Anthony Flesch. Risk-based Corrective Action Could Save Billions in LUST Cleanup Costs." *Environmental Solutions*, **9**(9):p. 32, 1996.
- ⁵ Vogel, Nancy. "Fuel Tank Danger Minimal, Study Says." *San Diego Union Tribune*, p. A-3, January 30, 1996.
- ⁴ O'Connor, Jeff and John Wollenberg. "Heap Pile Remediation is an Effective and Economical Method to Remediate Hydrocarbon Impacted Soil." *Navy Civil Engineer*, **34**(3): p. 8, 1995.
- ⁷ Labienic, Paula A., David A. Dzombak, and Robert L. Siegrist. "Risk Variability Due to Uniform Soil Remediation Goals." *Journal of Environmental Engineering*, **122**(7): p. 612, 1996.
- ⁸ Ames, Bruce N. and Lois Swirsky Gold. "The Causes and Prevention of Cancer." In *The True State of the Planet*, ed. R. Bailey. New York: Free Press, 1995., p. 142.
- ⁹ Kelly, Kathryn E. Presentation titled, "The Myth of 10^{-6} as a Definition of Acceptable Risk." Presented at the 84th Annual Meeting of the Air and Waste Management Association in Vancouver, B.C., Canada, June 1991., p. 6.
- ¹⁰ Kelly (1991), p. 6.
- ¹¹ Stephanatos, Basilis N. "How Clean is Clean? The Importance of Using Site-Specific Factors in Developing Cleanup Levels at Hazardous Waste Sites." In *Hydrocarbon Contaminated Soils*, eds. Paul T. Kostecki and Edward J. Calabrese. Chelsea, Mich: Lewis Publishers, 1991, p. 525.
- ¹² Rice, David W., Brendon P. Dooher, Stephen J. Cullen, Lorne G. Everett, William E. Kastenber, Randolph D. Grose and Miguel A. Marino. *Recommendations to Improve the Cleanup Process for California's Underground Fuel Tanks*. Livermore, Calif.: Lawrence Livermore National Laboratory (UCRL-AR-121762), 1995.

- ¹³ Pettit, Walt. Letter from the Executive Director of the California State Water Resources Control Board to all Regional Water Board Chairpersons, all Regional Water Board Executive Officers, and all Local Oversight Program (LOP) Agency Directors, dated December 8, 1995.
- ¹⁴ Bechtel National, Inc. *Draft Final Operable Unit 3A Remedial Investigation Report*. March 1997.
- ¹⁵ Bechtel National, Inc. (1997).
- ¹⁶ Englert, Christopher J., Earl J. Kenzie, and James Dragun. "Bioremediation of Petroleum Products in Soil." In *Petroleum Contaminated Soils*, eds. Edward J. Calabrese and Paul T. Kostecki. Chelsea, Mich: Lewis Publishers, 1993, p. 128.
- ¹⁷ Kampbell, Don H., T. H. Wiedemeier, and J. E. Hansen. "Intrinsic Bioremediation of Fuel Contamination in Ground Water at a Field Site." *Journal of Hazardous Materials*, **49**(2-3): p. 197, 1996.
- ¹⁸ Henry, Evan C. and Michael E. F. Hansen. "Letting the Sleeping Dog Lie: A Case Study in the No-Action Remediation Alternative for Petroleum Contaminated Soils." In *Petroleum Contaminated Soils*, eds. Edward J. Calabrese and Paul T. Kostecki. Chelsea, Mich: Lewis Publishers, 1993, p. 497.
- ¹⁹ Henry and Hansen (1993), p. 506.
- ²⁰ Arulanantham, Ravi and Atul Salhotra. *Risk and Decision Making at Petroleum Impacted Sites*. Emeryville, Calif: University of California Extension, 1996, p. 186.
- ²¹ Arulanantham and Salhotra (1996), p. 190.
- ²² Buscheck, Timothy E., David C. Wickland, and Donald L. Kuehne. "Multiple Lines of Evidence to Demonstrate Natural Attenuation of Petroleum Hydrocarbons." In *Proceedings of the Conference on Petroleum Hydrocarbons and Organic Chemicals in Groundwater*. National Groundwater Association/API, Houston, Texas, November 13-15, 1996.
- ²³ Metcalf & Eddy, Inc. *Chemical and Physical Characteristics of Crude Oil, Gasoline, and Diesel Fuel: A Comparative Study*. Santa Barbara, Calif. Submitted to Western States Petroleum Association. September 17, 1993. p. 4-7.
- ²⁴ Hemond, Harold E. and Elizabeth J. Fechner. *Chemical Fate and Transport in the Environment*. San Diego: Academic Press, 1994., pp. 36-37.
- ²⁵ Labieniec *et al.* (1996), p. 614.
- ²⁶ Metcalf & Eddy (1993), p. 4-17.

- ²⁷ Clark, Diane and Larry Hine. "Passive Remediation, Part 1." *Remediation Management*, 2(4): p. 40, 1996.
- ²⁸ Buscheck *et al.* (1996), p. 2.
- ²⁹ Kampbell *et al.* (1996), p. 198.
- ³⁰ Rice *et al.* (1995), p. 10.
- ³¹ Englert *et al.* (1993), p. 112.
- ³² Englert *et al.* (1993), p. 112.
- ³³ Metcalf & Eddy (1993), p. 4-17.
- ³⁴ Englert *et al.* (1993), p. 114.
- ³⁵ Englert *et al.* (1993), p. 112.
- ³⁶ Morin, Thomas C., "Enhanced Intrinsic Bioremediation Speeds Site Cleanup." *Pollution Engineering*. 29(2): p. 44, 1997.
- ³⁷ Frankenberger, Jr., W. T. and J. L. Newcomb. *Feasibility of Bioremediation in the Ex-Situ Clean-Up of Diesel Fuel at the Marine Corps Air Station El Toro, California*. Riverside, Calif: Center for Environmental Microbiology, December, 1995.
- ³⁸ Englert *et al.* (1993), p. 114.
- ³⁹ Englert *et al.* (1993), p. 114.
- ⁴⁰ O'Connor and Wollenberg (1995), p. 7.
- ⁴¹ Metcalf & Eddy (1993), p.2-4.
- ⁴² Gaudy, Jr., Anthony F. and Elizabeth T. Gaudy. *Elements of Bioenvironmental Engineering*. San Jose, California: Engineering Press, Inc., 1988, 430-431.
- ⁴³ Gaudy and Gaudy (1988), p. 432.
- ⁴⁴ Bell *et al.* (1991), p. 82.
- ²⁵ Frank, Michael. Telephone interview with Michael Frank of the Maryland Department of Environment, Waste Management Administration, Oil Control Program, on April 2, 1997.
- ⁴⁶ Dakins, Maxine E., John E. Toll, Mitchell J. Small, and Kevin P. Brand. "Risk-Based Environmental Remediation: Bayesian Analysis and the Expected Value of Sample Information." *Risk Analysis*, 16(1): p. 67, 1996.

Comprehensive References

Ames, Bruce N. and Lois Swirsky Gold. "The Causes and Prevention of Cancer." In *The True State of the Planet*, ed. R. Bailey. New York: Free Press, 1995.

Arulanantham, Ravi and Atul Salhotra. *Risk and Decision Making at Petroleum Impacted Sites*. Emeryville, Calif: University of California Extension, 1996.

Asante-Duah, Daniel Kofi. "Using a Risk Assessment Protocol to Develop Soil Cleanup Criteria for Petroleum Contaminated Sites." In *Hydrocarbon Contaminated Soils*, eds. Paul T. Kostecki and Edward J. Calabrese. Chelsea, Mich: Lewis Publishers, 1991, pp. 493-523.

Bechtel National, Inc. *DoD Petroleum Hydrocarbon Cleanup Demonstration Program, Expert Committee Briefing Package for Site 390*. January, 1997.

Bechtel National, Inc. *Draft Final Operable Unit 3A Remedial Investigation Report*. March, 1997.

Begley, Ronald. "Risk-based Remediation Guidelines Take Hold." *Environmental Science and Technology*, **30**(10):p. 438A, 1996.

Bell, Charles E., Paul T. Kostecki, and Edward J. Calabrese. "Review of State Cleanup Levels for Hydrocarbon Contaminated Soils." In *Hydrocarbon Contaminated Soils and Groundwater*, eds. Paul T. Kostecki and Edward J. Calabrese. Chelsea, Mich: Lewis Publishers, 1991, pp. 77-89.

Buscheck, Timothy E., David C. Wickland, and Donald L. Kuehne. "Multiple Lines of Evidence to Demonstrate Natural Attenuation of Petroleum Hydrocarbons." In *Proceedings of the Conference on Petroleum Hydrocarbons and Organic Chemicals in Groundwater*. National Groundwater Association/API, Houston, Texas, November 13-15, 1996.

Clark, Diane and Larry Hine. "Passive Remediation, Part 1." *Remediation Management*, **2**(4): p. 40, 1996.

Dakins, Maxine E., John E. Toll, Mitchell J. Small, and Kevin P. Brand. "Risk-Based Environmental Remediation: Bayesian Analysis and the Expected Value of Sample Information." *Risk Analysis*, **16**(1): p. 67, 1996.

Daugherty, Seth J. "Regulatory Approaches to Hydrocarbon Contamination from Underground Storage Tanks." In *Hydrocarbon Contaminated Soils and Groundwater*, eds. Paul T. Kostecki and Edward J. Calabrese. Chelsea, Mich: Lewis Publishers, 1991, pp. 23-59.

Englert, Christopher J., Earl J. Kenzie, and James Dragun. "Bioremediation of Petroleum Products in Soil." In *Petroleum Contaminated Soils*, eds. Edward J. Calabrese and Paul T. Kostecki. Chelsea, Mich: Lewis Publishers, 1993, pp. 111-129.

Everett, Lorne G. Technical Presentation titled, "Engineering Applications of Vadose Zone Hydrology Covering the Lawrence Livermore National Laboratory Hydrocarbon Reports." Presented at the Naval Facilities Engineering Command, Southwest Division, San Diego, Calif. on August 8, 1996.

Farr, John, George Apostolakis, Mike Collins, Robert Carrington Crouch III, Graham Fogg, Martin Reinhard, and Kate Scow. *Senate Bill 1764 Advisory Committee Recommendations Report Regarding California's Underground Storage Tank Program*. Submitted to the California State Water Resources Control Board, May 31, 1996.

Frank, Michael. Telephone interview with Michael Frank of the Maryland Department of Environment, Waste Management Administration, Oil Control Program, on April 2, 1997.

Frankenberger, Jr., W. T. and J. L. Newcomb. *Feasibility of Bioremediation in the Ex-Situ Clean-Up of Diesel Fuel at the Marine Corps Air Station El Toro, California*. Riverside, Calif: Center for Environmental Microbiology, December, 1995.

Gaudy, Jr., Anthony F. and Elizabeth T. Gaudy. *Elements of Bioenvironmental Engineering*. San Jose, California: Engineering Press, Inc., 1988.

Hemond, Harold E. and Elizabeth J. Fechner. *Chemical Fate and Transport in the Environment*. San Diego: Academic Press, 1994.

Henke, Steve. "Underground Storage Tanks: The environmental health role." *Journal of Environmental Health*, **56**(8): p. 13, 1994.

Henry, Evan C. and Michael E. F. Hansen. "Letting the Sleeping Dog Lie: A Case Study in the No-Action Remediation Alternative for Petroleum Contaminated Soils." In *Petroleum Contaminated Soils*, eds. Edward J. Calabrese and Paul T. Kostecki. Chelsea, Mich: Lewis Publishers, 1993, pp. 497-510.

Kampbell, Don H., T. H. Wiedemeier, and J. E. Hansen. "Intrinsic Bioremediation of Fuel Contamination in Ground Water at a Field Site." *Journal of Hazardous Materials*, **49**(2-3): p. 197, 1996.

Kangas, Michael. "Probabilistic Risk Assessment." *Standardization News*, **24**(6):p. 28, 1996.

Kelly, Kathryn E. Presentation titled, "The Myth of 10^{-6} as a Definition of Acceptable Risk." Presented at the 84th Annual Meeting of the Air and Waste Management Association in Vancouver, B.C., Canada, June 1991.

Kostecki, Paul T., Edward J. Calabrese, and Holly M. Horton. "Review of Present Risk Assessment Models for Petroleum Contaminated Soils." In *Petroleum Contaminated Soils*, eds. Edward J. Calabrese and Paul T. Kostecki. Chelsea, Mich: Lewis Publishers, 1993, pp. 553-590.

Labienic, Paula A., David A. Dzombak, and Robert L. Siegrist. "Risk Variability Due to Uniform Soil Remediation Goals." *Journal of Environmental Engineering*, **122**(7):p. 612, 1996.

Lide, David R., ed. *CRC Handbook of Chemistry and Physics.*, 75th edition, 1994.

McNab, Jr., Walt. W., Brendon P. Doohar, David W. Rice, Michael C. Kavanaugh, Paul C. Johnson, Stephen J. Cullen, Lorne G. Everett, William E. Kastenbergh, and Matthew C. Small. *Assessment of Appropriate Fuel Hydrocarbon Risk-Management Strategies for George Air Force Base, Victorville, California, Using a Risk-Based Approach.* Livermore, Calif.: Lawrence Livermore National Laboratory (UCRL-AR-125619), 1997.

Metcalf & Eddy, Inc. *Chemical and Physical Characteristics of Crude Oil, Gasoline, and Diesel Fuel: A Comparative Study.* Santa Barbara, Calif. Submitted to Western States Petroleum Association. September 17, 1993.

Metcalf & Eddy, Inc. *Wastewater Engineering: Treatment, Disposal and Reuse (Third Edition).* New York: McGraw-Hill, 1991.

Nakles, D. V., J. W. Lynch, D. Edwards, J. G. Tell, T. L. Potter, R. P. Andes, and C. P. L. Barkan, "Risk Based Management of Diesel-Contaminated Soil." Prepared by Remediation Technologies, Inc. for the Association of American Railroads, Environmental and Hazardous Materials Research Program, Research and Test Department, Washington, DC, October, 1996.

O'Connor, Jeff and John Wollenberg. "Heap Pile Remediation is an Effective and Economical Method to Remediate Hydrocarbon Impacted Soil." *Navy Civil Engineer*, **34**(3):p. 6, 1995.

Orange County Health Care Agency letter dated February 10, 1997.

Paustenbach, Dennis J., Renee Kalmes, James D. Jernigan, Rená Bass, and Paul Scott. "A Proposed Approach to Regulating Contaminated Soil: Identify Safe Concentrations for Seven of the Most Frequently Encountered Exposure Scenarios." In *Petroleum Contaminated Soils*, eds. Edward J. Calabrese and Paul T. Kostecki. Chelsea, Mich: Lewis Publishers, 1993, pp. 511-552.

Pettit, Walt. Letter from the Executive Director of the California State Water Resources Control Board to all Regional Water Board Chairpersons, all Regional Water Board Executive Officers, and all Local Oversight Program (LOP) Agency Directors, dated December 8, 1995.

Phillips, J. B., M. A. Hindawi, A. Phillips, and R. V. Bailey. "Imperfect Choices: Transfers from Liquid and Vapor Media." *Pollution Engineering*, **29**(7):p. 39, 1997.

Rapaport, Diane, and Anthony Flesch. Risk-based Corrective Action Could Save Billions in LUST Cleanup Costs." *Environmental Solutions*, **9**(9):p. 28, 1996.

Rice, David W., Brendon P. Dooher, Stephen J. Cullen, Lorne G. Everett, William E. Kastenberg, Randolph D. Grose and Miguel A. Marino. *Recommendations to Improve the Cleanup Process for California's Underground Fuel Tanks*. Livermore, Calif.: Lawrence Livermore National Laboratory (UCRL-AR-121762), 1995.

Rounds, Dennis D. and Paul C. Johnson. "Risk-Based Corrective Action at Petroleum Release Sites." *Standardization News*, **22**(5):p. 30, 1994.

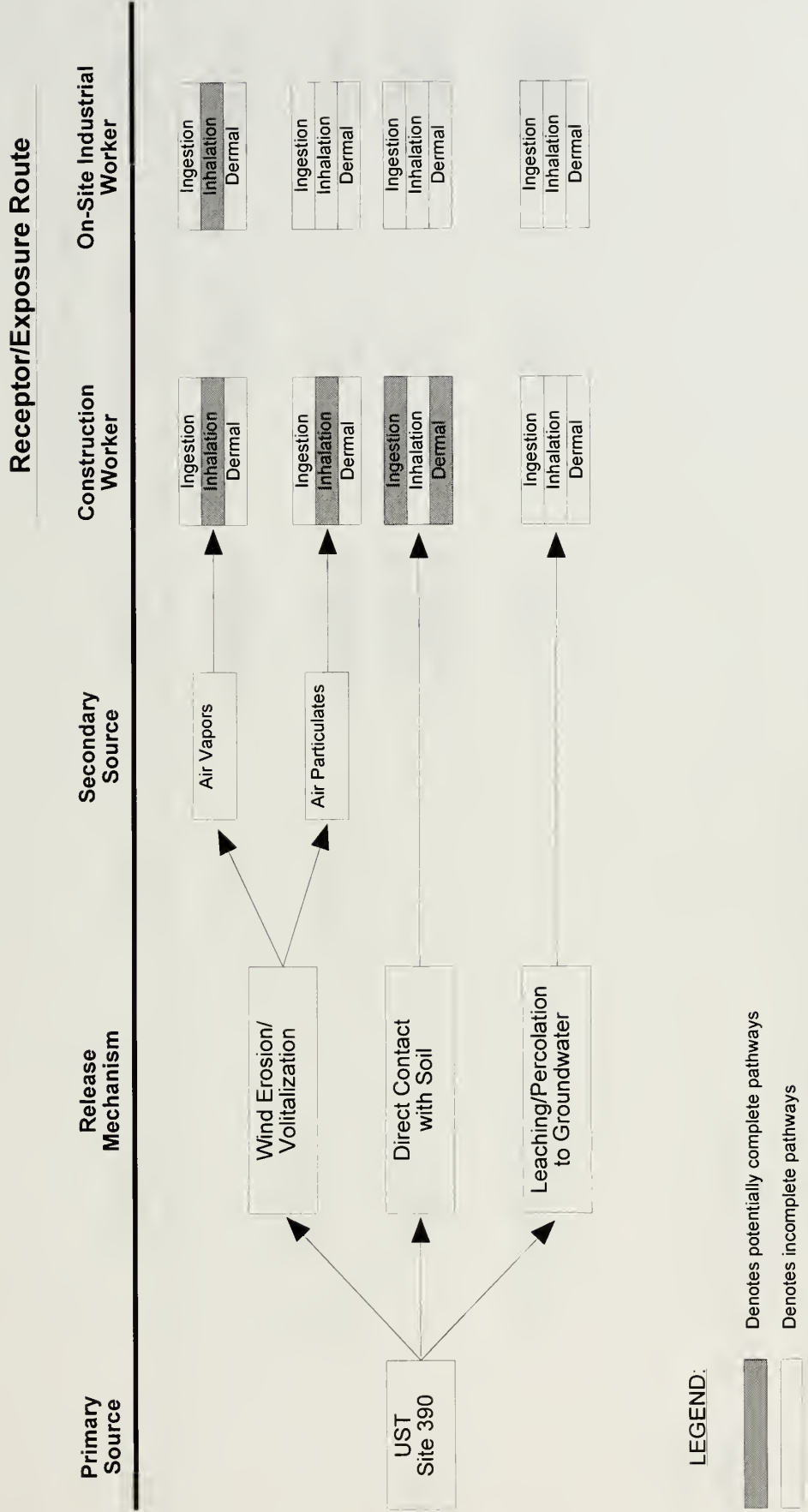
Stanley, Curtis C. and Paul C. Johnson. "Risk-Based Corrective Action." *Standardization News*, **24**(6):p. 22, 1996.

Stephanatos, Basilis N. "How Clean is Clean? The Importance of Using Site-Specific Factors in Developing Cleanup Levels at Hazardous Waste Sites." In *Hydrocarbon Contaminated Soils*, eds. Paul T. Kostecki and Edward J. Calabrese. Chelsea, Mich: Lewis Publishers, 1991, p. 525.

University of Wisconsin-Madison. *Underground Tank Technology Update*, **10**(3), 1996.

Vogel, Nancy. "Fuel Tank Danger Minimal, Study Says." *San Diego Union Tribune*, p. A-3, January 30, 1996.

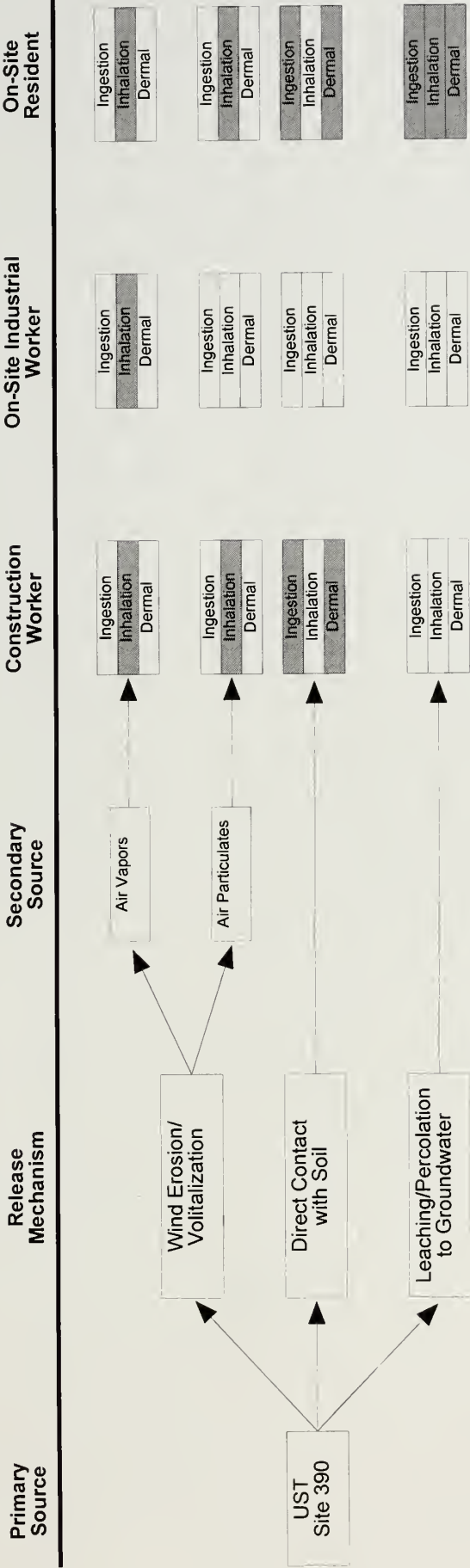
Site Conceptual Exposure Scenario under Current Conditions



NOTES: Construction workers are assumed to be exposed to soils up to 10 feet below ground surface. Exposure of On-Site Industrial workers is limited due to asphalt pavement cover at the site which prevents wind erosion and direct contact with the soil.

Site Conceptual Exposure Scenario under Possible Future Conditions

Receptor/Exposure Route



LEGEND:

- Denotes potentially complete pathways
- Denotes incomplete pathways

NOTES:

Construction workers are assumed to be exposed to soils up to 10 feet below ground surface
Exposure of On-Site Industrial workers is assumed to be limited due to asphalt pavement cover remaining in place at the site which prevents wind erosion and direct contact with the soil
On-Site Residents are assumed to use water from an on-site well for domestic purposes. Site is assumed to be unpaved.

11 5INPS
TH
1/99 22527-200 11016



DUDLEY KNOX LIBRARY



3 2768 00356569 8